

Introduction:

Phosphate mobility has been postulated as an indicator of early aqueous activity on Mars [1]. In addition, rock surfaces analyzed by the Mars Exploration Rover Spirit are consistent with the loss of a phosphate-containing mineral [2]. To interpret phosphate alteration behavior on Mars, we performed column dissolution experiments leaching the primary phases Durango fluorapatite, San Carlos olivine, and basalt glass (Stapafjell Volcano, courtesy of S. Gislason, University of Iceland) [3,4]) with acidic solutions. These phases were chosen to represent quickly dissolving phases likely present in Columbia Hills. Column dissolution experiments are closer to natural dissolution conditions than batch experiments, although they can be difficult to interpret. Acidic solutions were used because the leached layers on the surfaces of these rocks have been interpreted as resulting from acid solutions [5].

Methods: Eight columns were prepared, four in a Coy glove box which was continually purged with high purity N₂ (“anoxic”), and four on the laboratory bench top (“oxic”). Each column contained a mixture of 1.5 g each of powdered, sieved and washed Durango fluorapatite, Stapafjell glass, and San Carlos olivine. Each condition (oxic or anoxic) contained 4 different solutions: 0.001 N HCl, 0.001 H₂SO₄, 0.1 N HCl, and 0.1 N H₂SO₄. For all solutions MilliQ water and trace element grade acids were used. Acid concentrations were determined by titration against a known concentration of base, and pH measurements were performed on input solutions. All solutions were bubbled with N₂ for at least 40 minutes before placing in the Coy glove box.

Output solutions were measured for pH, filtered with a 0.45 µm filter, acidified with trace element grade HNO₃ to 1% and then analyzed for the cations Ca, Mg, Na, Al, Si, Ti, and Fe by atomic absorption, and for sulfate, chloride, phosphate and fluoride by ion chromatography. In some cases the filters were saved, and examined by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and X-Ray Diffraction (XRD). Visual precipitates were optically observed in some samples of output solutions, and were prepared by centrifuging and then freeze drying for analysis by XRD. At the end of the experiments, columns were flushed with deionized water, and then freeze dried, weighed, and analyzed by SEM, EDS and XRD. Experiments were run for ~350 hrs,

and sampled at least every 72 hours. The first sample was discarded to prevent dilution by deionized water.

Results and Discussion:

Leached primary phases.

The columns reacted with the higher concentrations of acid were visibly bleached compared to the columns reacted with the lower concentration acids (Figure 1). Since mineral changes were more extensive in the columns leached with the more concentrated acids (0.1M), we focus on those columns here. When the heavily leached columns were weighed at the end of the experiment, each column contained less than 1.25g of material, compared with the 4.5 g of starting material.



Figure 1. Photo of columns at end of experiment.

Bleached columns A2 & O2 were reacted with 0.1M HCl and A4 & O4 with 0.1M H₂SO₄. Unbleached columns A1 & O1 were leached with 0.001 HCl and A3 & O3 were leached with 0.001 H₂SO₄ (A for “oxic” and O for “anoxic”)

lated based on measured flow rates and concentrations. The percentage of Ti removed was found to be less than 5% in all columns, compared to losses of greater than 50% in the heavily acidic columns of elements such as Ca, Mg, Fe, and Na. This suggests that under these Mars-like conditions, Ti may not be very mobile.

Secondary minerals formed

Precipitates formed in the output solutions were visibly observed (Figure 2).



Figure 2. Photograph of precipitates in output solutions. Solutions are from “oxic” columns of the figure 1. A similar trend was seen for the anoxic columns.

Precipitates on the 0.45 μm filters were observed by SEM and EDS (Figure 3), and by XRD. Precipitates consisted of a Ca-sulfate in the sulfuric acid-containing columns, and (sulfuric-acid containing columns), and aluminum phosphate (sulfuric acid and hydrochloric acid-containing columns).

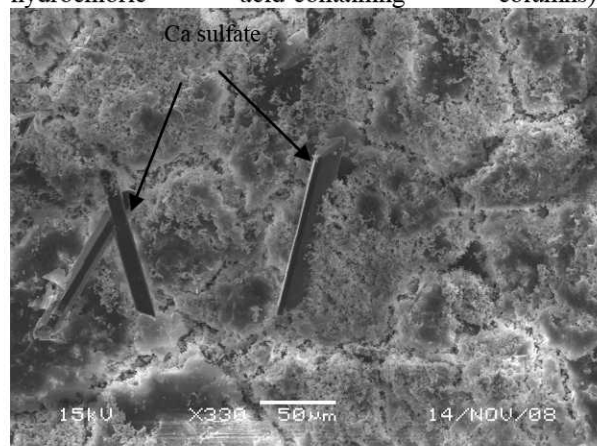


Figure 3. SEM image of a carbon-coated filter from a column containing 0.1 M sulfuric acid. Angular crystals are calcium sulfate, identified as gypsum by XRD. The amorphous mass is aluminum phosphate, which is amorphous when analyzed by XRD.

Secondary precipitates collected by centrifugation followed by freeze-drying were analyzed by XRD, and gypsum (columns containing sulfuric acid) and an amorphous phase, assumed to be aluminum phosphate were detected. This suggests that an amorphous aluminum phosphate phase, which may ripen to a crystalline aluminum phosphate phase, may be present on the surface of Mars. This is consistent with previous iden-

tifications of an aluminum phosphate phase by the Mini-TES on the Mars Exploration Rover Spirit [6].

Conclusions:

The heavily leached material inside the columns consists largely of Si and Ti, with a loss of less than 5% of the original Ti in all cases, compared with extensive loss of original minerals overall (>70% loss by mass). The Si and Ti-rich material may be similar to Si and Ti-rich deposits found on Mars [7,8]. Both Ca and P-containing secondary phases formed, suggesting that Ca and P loss reflects both mineral dissolution as well as secondary mineral formation. Secondary minerals include an amorphous aluminum phosphate phase, consistent with previous identifications of an aluminum phosphate phase by TES [6] and gypsum.

Further work will include mineral dissolution rates of the constituent minerals based on these column experiments, to determine the kinetic mineral dissolution rates under these conditions, with implications for the duration and characteristics of liquid water on Mars.

References:

- [1] Greenwood J.P and Blake R.E. (2006) *Geology*, 34, 953-956. [2] Hurowitz J.A. *et al* (2006) *JGR*, 111, E02S19 [3] Oelkers E.H. and Gislason S.R. (2001) *GCA*, 65, 3671-3681 [4] Gislason S.R. and Oelkers E.H. (2003) *GCA* 67, 3817-3832. [5] Hurowitz, J.A. *et al.* (2006) *JGR*, 111, E12S14 [6] Ruff, S.W. *et al.* (2006) *JGR*, 111, E12S18 [7] Squyres, S.W. *et al.* (2007) *Science*, 316, 1738 [8] Squyres, S.W. *et al* (2008) *Science*, 320, 1063, 2008